Chemical Kinetics

HYEG + HYEP + HYET
Programs

EXPLANATION OF KINETIC TERMS

KINETICS

- The word "*kinetic*" was originally used to mean 'pertaining to motion'. For example, the kinetic theory of gases deals with properties of gases which are dependent on molecular motion.
- ***In chemical reactions there is no motion, but there are changes in concentrations.*** The phrase 'chemical kinetics', which is often abbreviated to 'kinetics', is used to describe the ***quantitative study of concentration changes with time, due to chemical reactions***.

CLASSIFICATION OF REACTIONS

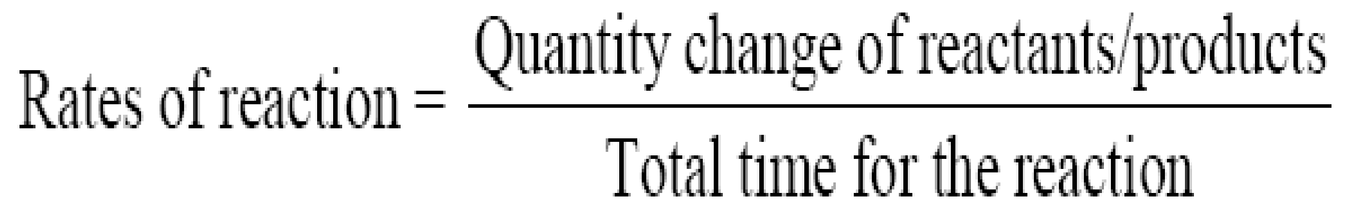
- Chemical reactions can be divided into two broad *categories*—*homogeneous* and *heterogeneous*. In the former case only one phase is present and the system is uniform in composition throughout. Reactions in a single solvent in which no solid catalyst is used are homogeneous. So, too, are gas reactions that do not involve catalysts or free radicals. Some examples of homogeneous reactions are
- $H_2 + I_2 \rightarrow 2HI$ (in the gas phase)
- $CH_3COCl + CH_3OH \rightarrow CH_3CO.OCH_3 + HCl$ (in the liquid phase)

- In heterogeneous reactions the mixture is not uniform throughout, and reaction occurs at phase boundaries. This is typically the case when solid catalysts are used as in the following examples.
- $C_2H_5OH \xrightarrow{\text{alumina}} C_2H_4 + H_2O$
- $2NH_3 \xrightarrow{\text{tungsten}} N_2 + 3H_2$
- The *order of reaction*, as will be explained later, is also used to classify chemical reactions in accordance with their kinetic behavior.

RATE OF REACTION

- The precise meaning of the term ‘rate of reaction’ is not self-evident. ***A simple definition would be the mass of product formed in a given time under stated conditions***.

- The **reaction rate** or **rate of reaction** for a reactant or product in a particular reaction is intuitively defined as how fast a reaction takes place.



$$\text{Rates of reaction} = \frac{\text{Quantity change of reactants/products}}{\text{Total time for the reaction}}$$

Examples

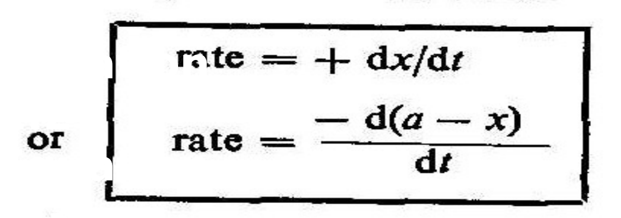
Wood Burning (2)
.A chemical rxn with a fast rxn rate

Iron Rusting (1)
a chemical rxn with a slow rxn -rate

- However, two objections to this interpretation:
  (a) the concentration of reactants changes as the reaction proceeds, and hence constant conditions cannot be maintained,
  (b) the amount of product formed depends on the initial quantity of reactants as well as on their concentrations and chemical reactivities.
  These difficulties are overcome by defining the ***rate of reaction*** as the ***decrease in concentration per unit time of one of the reactants*****.**
  Concentrations are usually expressed in moles per litre; the time in minutes or seconds.

- This definition may be expressed more concisely using the notation of the differential calculus. If [A] represents the concentration of the reactant A, measured at time t, then the rate is defined as

  $\text{rate} = - d[A]/dt$ *Equation 1;1*
- The minus sign occurs because the concentration of the reactant *decreases* with increasing time. An alternative definition of the rate of reaction is in terms of the product.
- If (*a*) represents the initial concentration of A and (x) represents the concentration of product at time (t) then:



$$\text{rate} = +\,dx/dt$$

or

$$\text{rate} = \frac{-\,d(a-x)}{dt}$$

,

1.3

in (1.2) the sign is positive since the concentration products *increases* with time.

:Consider a typical chemical reaction-

$$aA + bB \rightarrow pP + qQ$$

The lowercase letters (*a*, *b*, *p*, and *q*) represent stoichiometric coefficients, while the capital letters represent the reactants (A and B) and the products (P and Q).

According to the IUPAC's Gold Book definition[1] the reaction rate *r* for a chemical reaction occurring in a closed system under constant-volume conditions, without a build-up of reaction intermediates, is defined as:

$$r = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = \frac{1}{p}\frac{d[P]}{dt} = \frac{1}{q}\frac{d[Q]}{dt}$$

RATE CONSTANT

- *(Alternative names are rate coefficient or specific reaction rate. Usual symbol is k)*
- **The rate constant is a measure of the rate of a given chemical reaction under specified conditions**. It may be defined in words as ***the change in concentration of reactant or product per unit time in a reaction in which all the reactants are at unit concentration.*** The definition is helpful in that it gives some physical meaning to the rate constant.

- As an example, in the decomposition of benzene diazonium chloride in water

$$C_6H_5N_2C1 + H_20 \rightarrow C_6H_5OH + N_2 + HC1$$

- the rate constant is 4.24 x $l0^{-4}$ at 40°C. From the definition, in one litre of a one molar solution, 4.24 x $l0^{-4}$ moles of benzene diazonium chloride will react in one second at this temperature. It follows also that if the unit of time used in measuring the rate constant is changed from seconds to minutes, the rate constant will increase by a factor of sixty.

- The above definition of rate constant cannot always be used quantitatively because:
  (a) chemical reactions are not, in general, carried out with all the reactants at one mole per litre; indeed many reactants are not soluble to this extent.
  (b) even if the system were initially at unit concentration, as soon as reaction occurred the concentrations would alter. Hence the definition is valid only where the amount of reaction in unit time is small.

- In order to obtain a precise definition, applicable to all cases, the calculus notation must be used. At constant temperature the rate of reaction depends upon the concentrations of the reactants, although it is not always directly proportional to them as would be implied by the law of mass action. In more formal language:
  rate of reaction = a constant multiplied by a function of the concentrations of reactants

  $$dx/dt = k \times f(a,b,c,\ldots) \qquad 1.4$$

  where ***k*** is the rate constant and ***a, b, c,*** . . . represent the concentrations of the reactants A, B, C,... at time *t*. The function ***f(a, b,, c,...)*** represents some mathematical expression that is a characteristic of the reaction.

- This function only involves the products of the concentrations, each raised to a certain power, and so it becomes unity when all the reactants are at unit concentration since ln = 1, Under these conditions, therefore, *dx/dt* = ***k*****,** which is the rate constant in agreement with the earlier definition. For a given reaction, the value of ***k*** is constant at a constant temperature, and is a convenient quantitative measure of chemical reactivity. It must be stressed, however, that ***k*** increases rapidly with temperature, and so equations like (1.4) are only valid when the temperature is kept constant.
- $dx/dt = k \times f(a,b,c,\ldots)$ 1.4

For example, the rate of the reaction **$2\ NO + O_2 = 2\ NO_2$**
has the form:
***Rate* = *k* $[O_2]\ [NO]^2$**

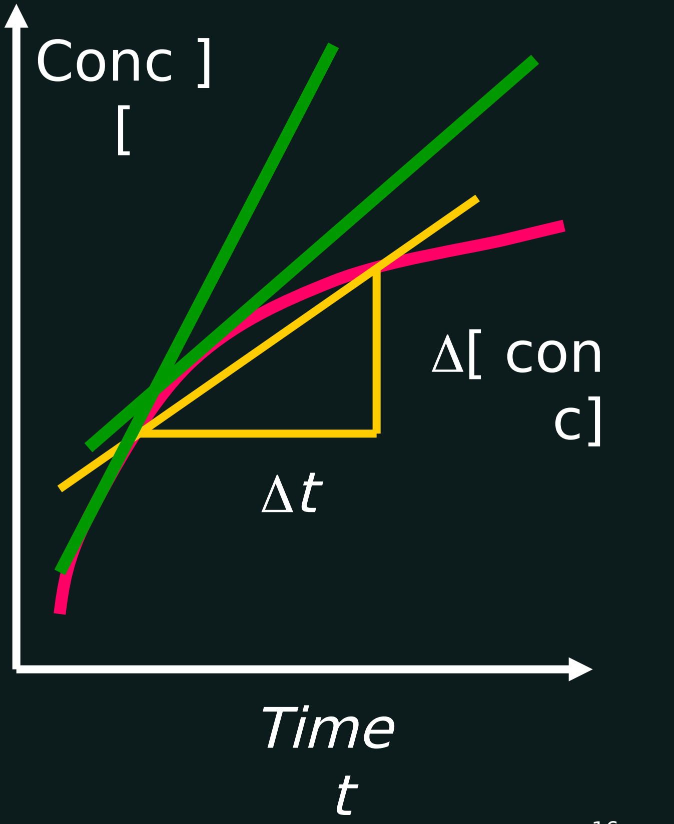
Reaction Rate Defined

:Reaction Rate
Changes in concentration of a product or a reactant per unit time

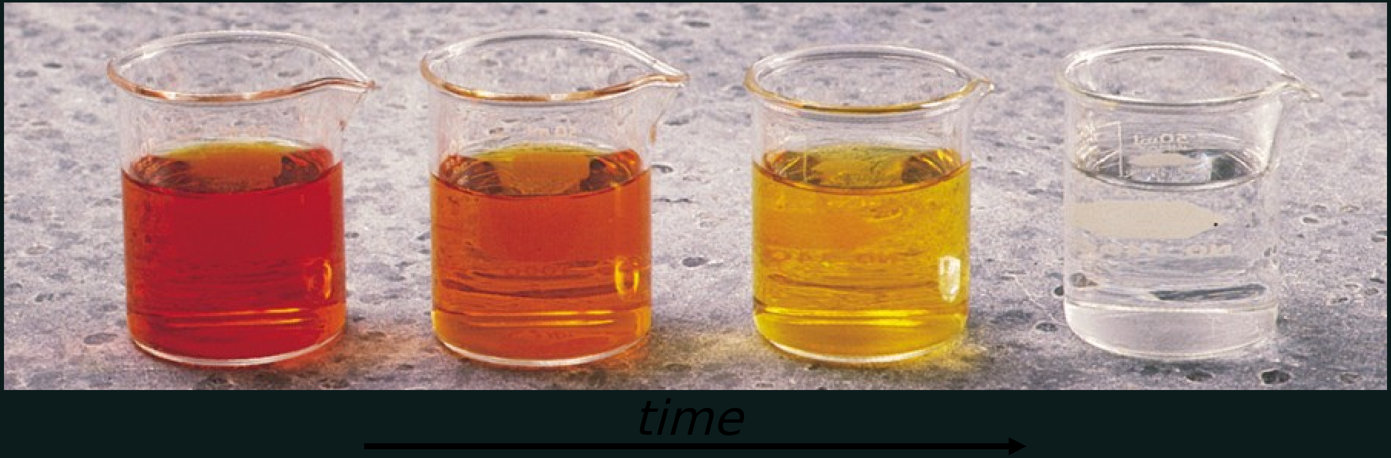
Δ[concentration]
=Reaction Rate
Δt

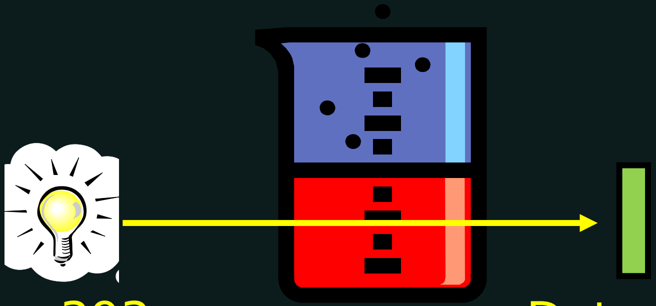
Delta= change

Note that the slope changes with time

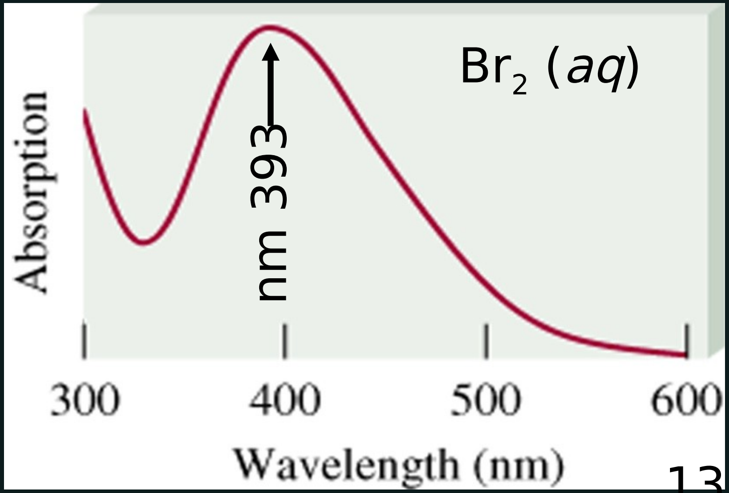


$Br_2\ (aq) + HCOOH\ (aq) \longrightarrow 2Br^-\ (aq) + 2H^+\ (aq) + CO_2\ (g)$

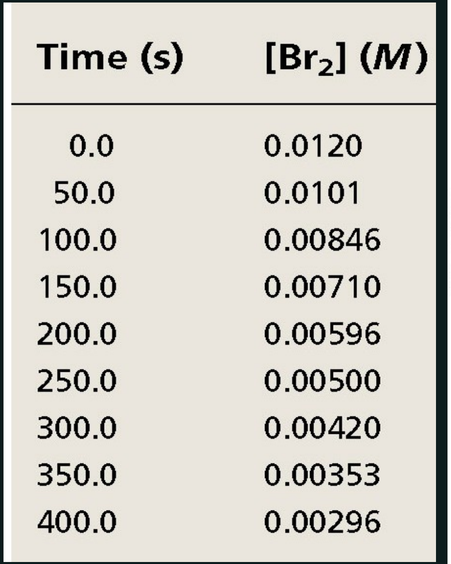




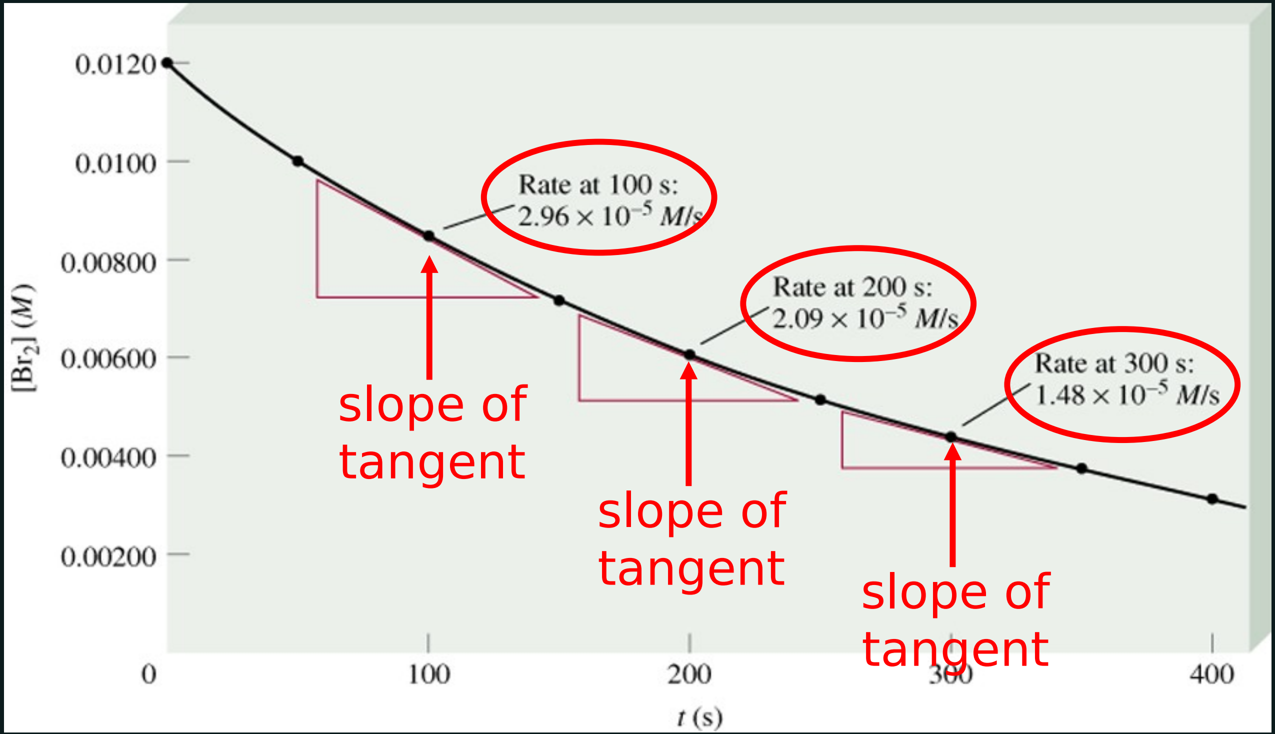
$\Delta[Br_2]\ \alpha\ \Delta$ Absorption



$Br_2\ (aq) + HCOOH\ (aq) \longrightarrow 2Br^-\ (aq) + 2H^+\ (aq) + CO_2\ (g)$



Time (s)	$[Br_2]$ (*M*)
0.0	0.0120
50.0	0.0101
100.0	0.00846
150.0	0.00710
200.0	0.00596
250.0	0.00500
300.0	0.00420
350.0	0.00353
400.0	0.00296



$- =$ ***average rate*** $\dfrac{\Delta[Br_2]}{\Delta t}$ $- =$ $\dfrac{{}_{\text{final}} - [Br_2]_{\text{initial}}[Br_2]}{t_{\text{final}} - t_{\text{initial}}}$

instantaneous rate = rate for specific instance in time

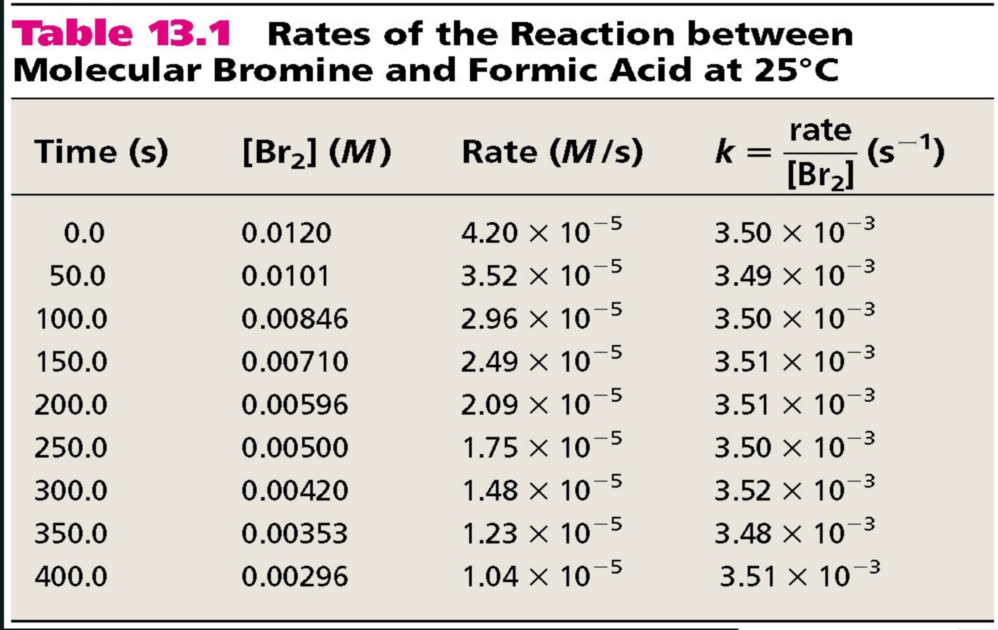


Table 13.1 **Rates of the Reaction between Molecular Bromine and Formic Acid at 25°C**

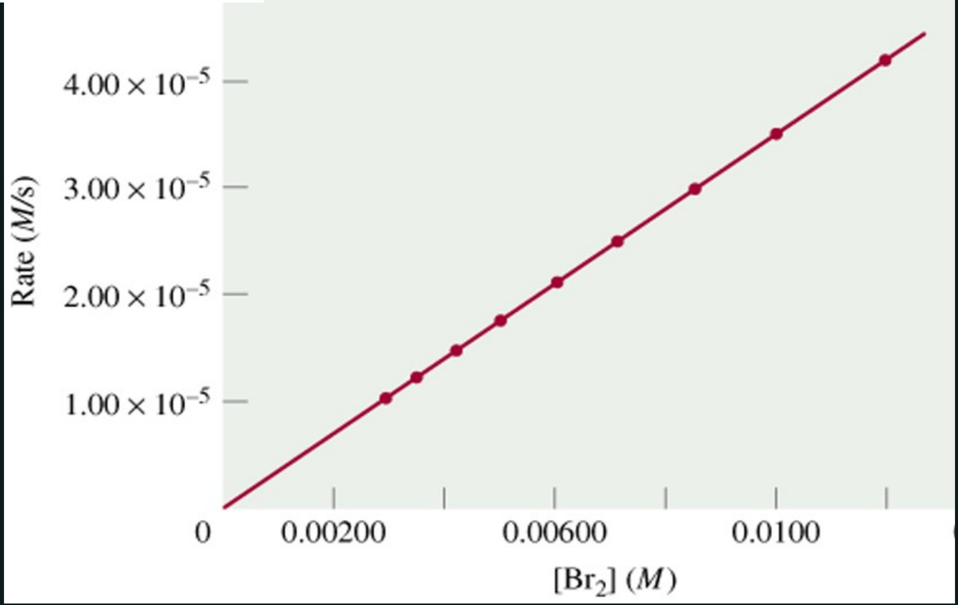
Time (s)	$[Br_2]$ (*M*)	Rate (*M*/s)	$k = \frac{\text{rate}}{[Br_2]}$ (s^{-1})
0.0	0.0120	4.20×10^{-5}	3.50×10^{-3}
50.0	0.0101	3.52×10^{-5}	3.49×10^{-3}
100.0	0.00846	2.96×10^{-5}	3.50×10^{-3}
150.0	0.00710	2.49×10^{-5}	3.51×10^{-3}
200.0	0.00596	2.09×10^{-5}	3.51×10^{-3}
250.0	0.00500	1.75×10^{-5}	3.50×10^{-3}
300.0	0.00420	1.48×10^{-5}	3.52×10^{-3}
350.0	0.00353	1.23×10^{-5}	3.48×10^{-3}
400.0	0.00296	1.04×10^{-5}	3.51×10^{-3}

rate α $[Br_2]$

rate = $k\,[Br_2]$

$= k \frac{\text{rate}}{[Br_2]}$ ***rate constant =***

x 10^{-3} s^{-1} 3.50 =



The Rate Law

- The ***rate law*** expresses the relationship of the rate of a reaction to the rate constant and the concentrations of the reactants raised to some p

$$aA + bB \longrightarrow cC + dD$$

$$\text{Rate} = k\,[A]^x[B]^y$$

reaction is ***x*th order** in A

reaction is ***y*th order** in B

reaction is **(x +y)th order overall**

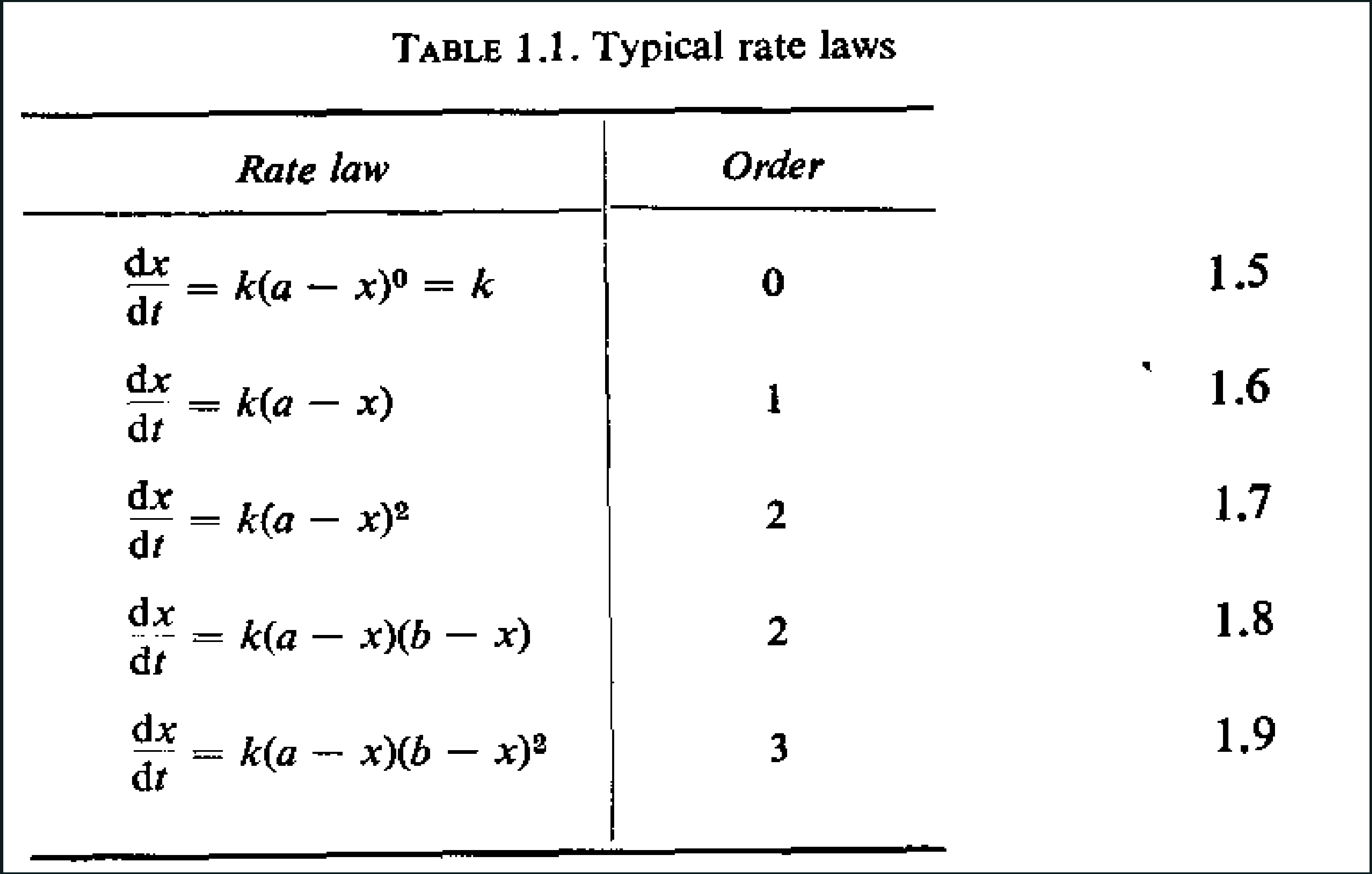


TABLE 1.1. Typical rate laws

Rate law	*Order*	
$\frac{\mathrm{d}x}{\mathrm{d}t} = k(a - x)^0 = k$	0	1.5
$\frac{\mathrm{d}x}{\mathrm{d}t} = k(a - x)$	1	1.6
$\frac{\mathrm{d}x}{\mathrm{d}t} = k(a - x)^2$	2	1.7
$\frac{\mathrm{d}x}{\mathrm{d}t} = k(a - x)(b - x)$	2	1.8
$\frac{\mathrm{d}x}{\mathrm{d}t} = k(a - x)(b - x)^2$	3	1.9

ORDER OF REACTION

- The word ‘order’ is used in pure mathematics in the classification of differential equations. The rate laws shown in TABLE 1.1 are all differential equations. In chemical kinetics, these equations are classified according to the *order of reaction.*
- The order is usually ***a small whole number***, but in special cases it may have a fractional value or be zero, It is formally ***defined as the sum of the powers of the concentration terms that occur in the differential form of the rate law***. Thus a reaction with rate law (1.6) is first order since the concentration term is raised to the power of unity. (1.7) and (1.8) are second order and (1.9) is third order.

- Since any number to the power of zero equals one, (1.5) may be written dx/dt = $k(a - x)^{\circ}$ and is, therefore, of zero order. Rate laws and corresponding orders are shown in TABLE 1.1. It cannot be too strongly emphasized that the *order* of reaction is ***entirely an experimental quantity.*** It can be measured experimentally without any prior knowledge of the mechanism of the reaction. This follows from the fact that the order is determined by finding out which rate law best fits the experimental data. The order can *not* be found by looking at the chemical equation for the reaction. Finally, it must not be confused with *molecularity* which is defined as follows.

Rates as Functions of Reactant Concentrations

:Example

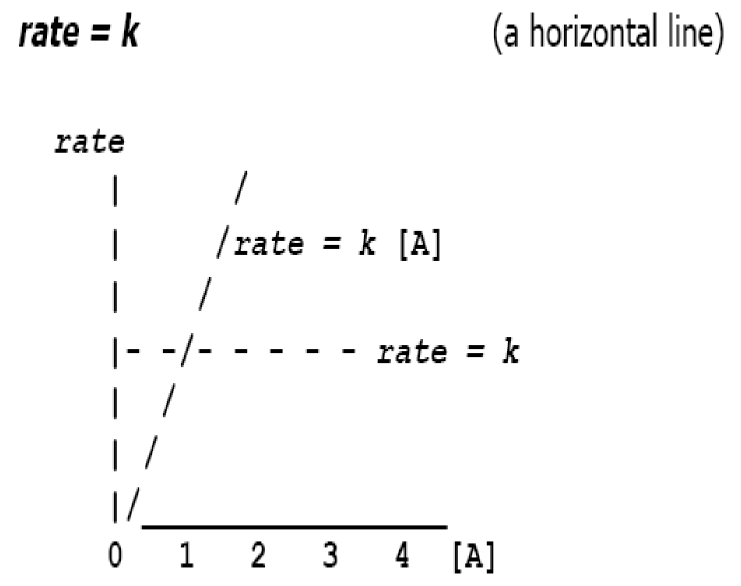
a A + b B + c C = products

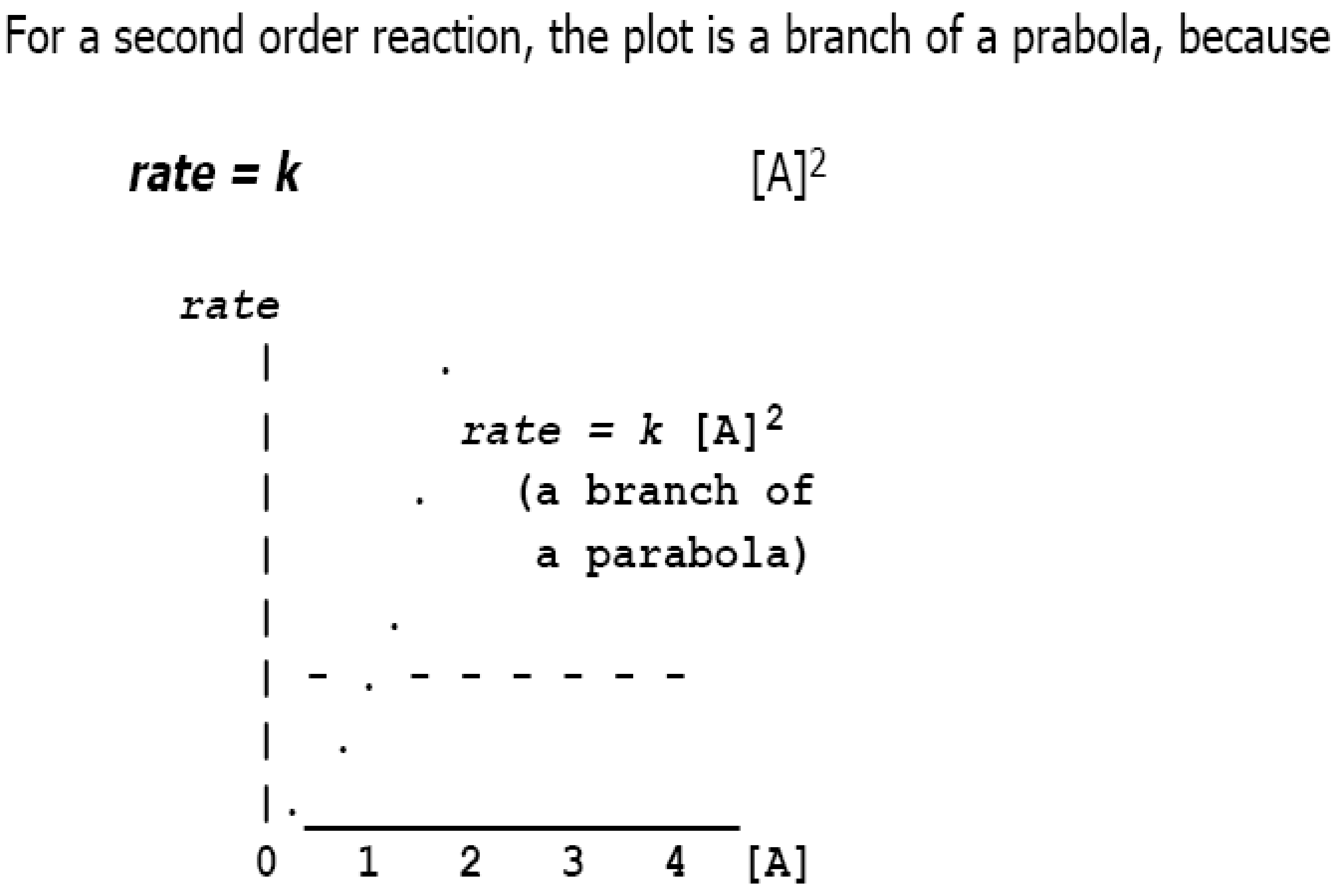
If concentrations of B and C are kept constant, you can measure the reaction **rate** of .A at various concentrations

For a zeroth order reaction, .you will get a horizontal line

For a first order reaction, the ,plot is a straight line (linear) as shown above, because

rate = k [A] (a straight line



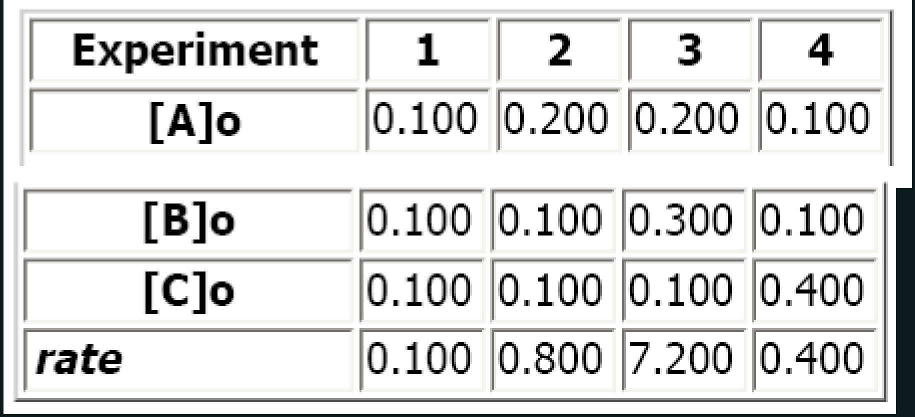


For a second order reaction, the plot is a branch of a prabola, because

$rate = k$ $[A]^2$

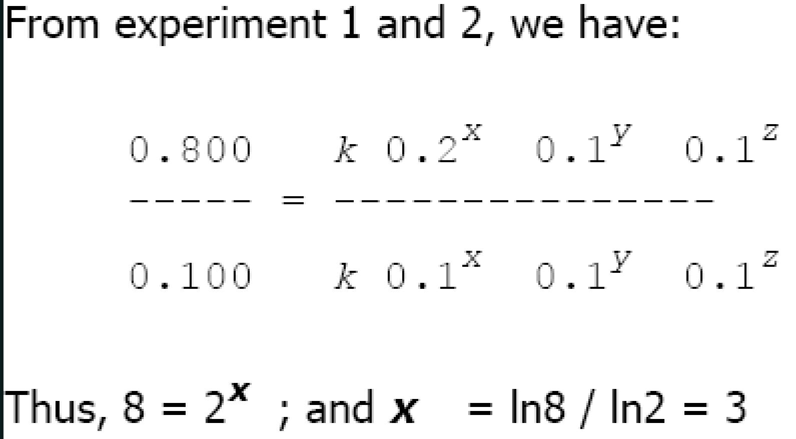
Evaluation of order by Experiments

- **Example:**
- **Derive the rate law for the reaction A + B + C => products from the following data, where *rate* is measured as soon as the reactants are mixed.**



Experiment	**1**	**2**	**3**	**4**
[A]o	0.100	0.200	0.200	0.100
[B]o	0.100	0.100	0.300	0.100
[C]o	0.100	0.100	0.100	0.400
rate	0.100	0.800	7.200	0.400

- ***Solution***
  Assume the orders to be *x*, *y*, and *z* respectively for A, B, and C, we have
- ***rate* = *k* [A]^x [B]^y [C]^z**



From experiment 1 and 2, we have:

$$\frac{0.800}{0.100} = \frac{k\ 0.2^x\ \ 0.1^y\ \ 0.1^z}{k\ 0.1^x\ \ 0.1^y\ \ 0.1^z}$$

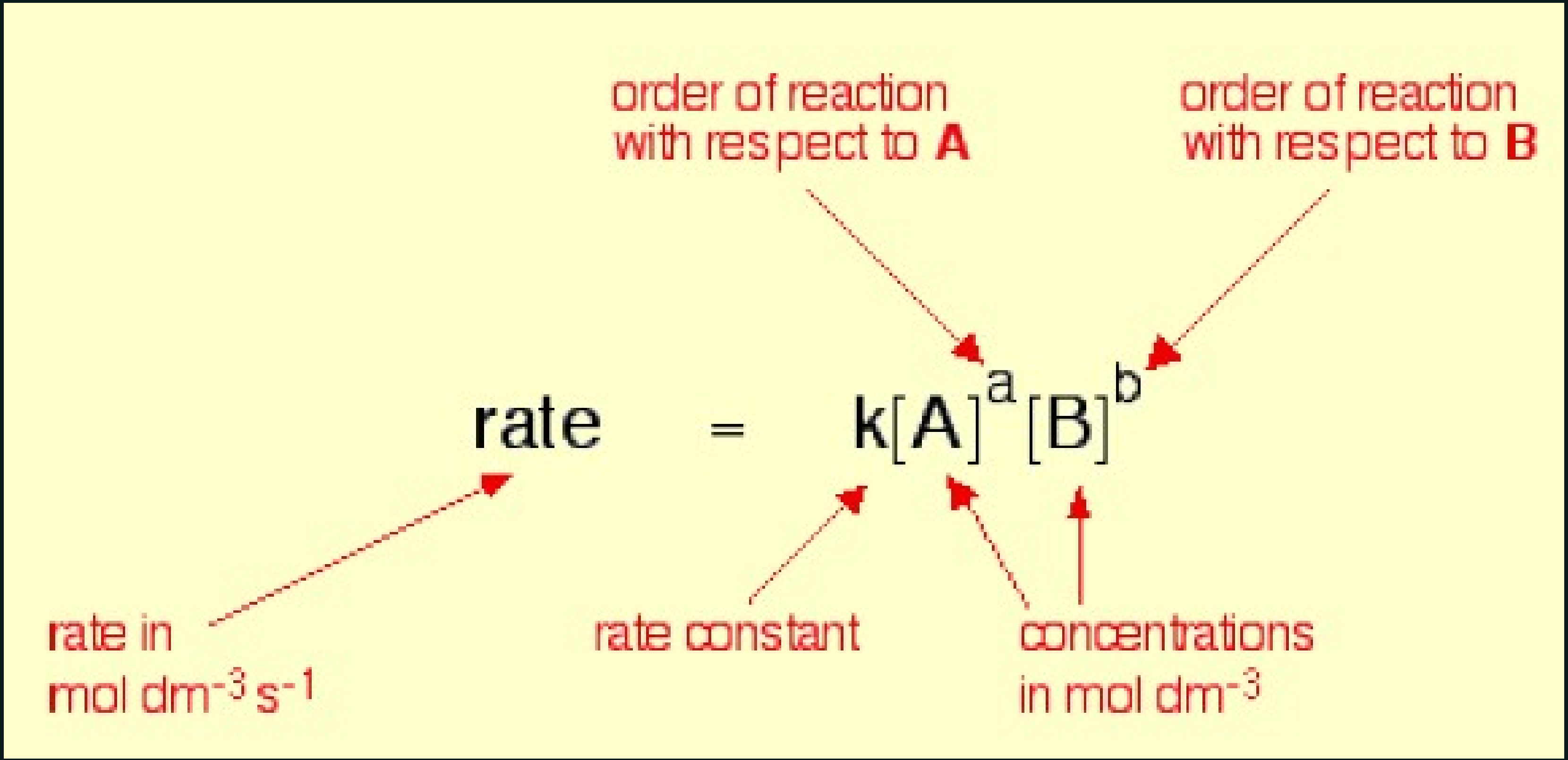
Thus, $8 = 2^{\boldsymbol{x}}$; and $\boldsymbol{x} = \ln 8 / \ln 2 = 3$

rate = *k* [A]^3 [B]^2 [C]

y = 2 and z = 1

Summary

rate equation



order of reaction with respect to **A**

order of reaction with respect to **B**

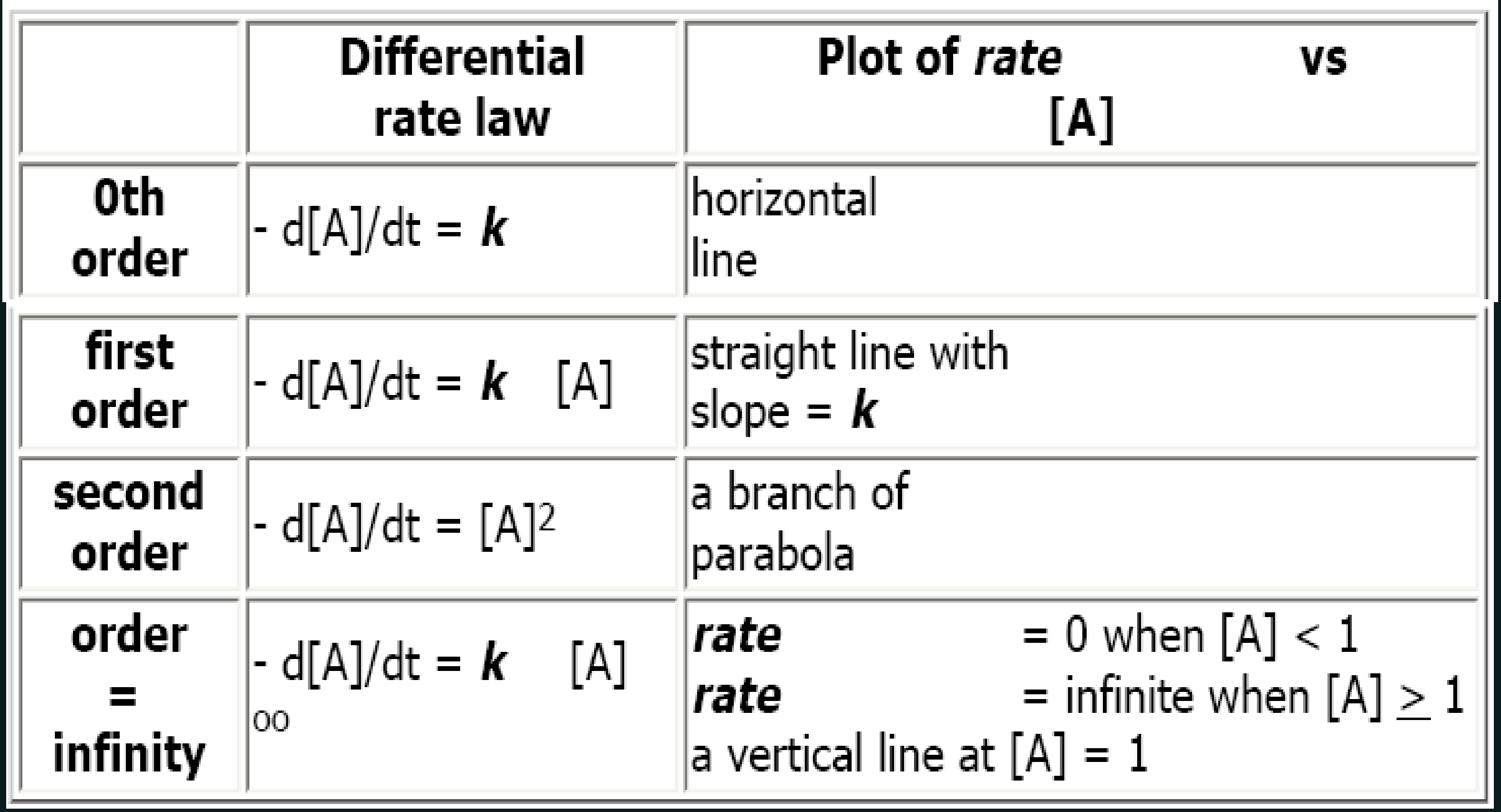
$$\text{rate} = k[A]^a[B]^b$$

rate in mol dm^{-3} s^{-1}

rate constant

concentrations in mol dm^{-3}

Summary cont.



	Differential rate law	Plot of *rate* vs [A]
0th order	- d[A]/dt = ***k***	horizontal line
first order	- d[A]/dt = ***k*** [A]	straight line with slope = ***k***
second order	- d[A]/dt = $[A]^2$	a branch of parabola
order = infinity	- d[A]/dt = ***k*** [A] oo	***rate*** = 0 when [A] < 1 ***rate*** = infinite when [A] ≥ 1 a vertical line at [A] = 1

POP BRAIN

If the reaction *rate* doubles as the concentration of .1 the reactant A increase by a factor of 2, what is the ?order of the reaction with respect to A

If the reaction *rate* is a constant as the .2 concentration of a reactant A varies, what is the ?order of the reaction with respect to A

For a reaction that is 2nd order with respect to A, you .3 can keep concentrations of other reactants constant, and vary the concentration of A. You can measure the initial *rate* in the experiments, and then plot *rate* as a ?function of [A]. What type of curve or line is such a plot

Examples

,In the following decomposition reaction .1

$$N_2O_5 \rightarrow 4\ NO_2 + O_2\ 2$$

oxygen gas is produced at the average rate of 9.1×10^{-4} mol · L^{-1} · s^{-1}. Over the same period, what is the average :rate of the following

- i) the production of nitrogen dioxide
- ii) the loss of nitrogen pentoxide

:Consider the following reaction .2

$$N_2(g) + 3\ H_2(g) \rightarrow 2\ NH_3(g)$$

If the rate of loss of hydrogen gas is 0.03 mol · L^{-1}· s^{-1}, ?what is the rate of production of ammonia

MOLECULARITY OF REACTION

- The strength of a chain cannot exceed the strength of the weakest link. There is a corresponding principle in kinetics, namely that the overall rate of a process cannot exceed the rate of the slowest stage. This ‘bottleneck principle’ is frequently observed in everyday life. For instance, if a large crowd is leaving a building which has only a few small exits (such as a theatre or cinema), the time taken to empty the building is determined by the number of people who can squeeze through the doors per second. Whether people run or walk to the doors makes no difference to the rate of leaving; it merely affects the size of the queue inside.

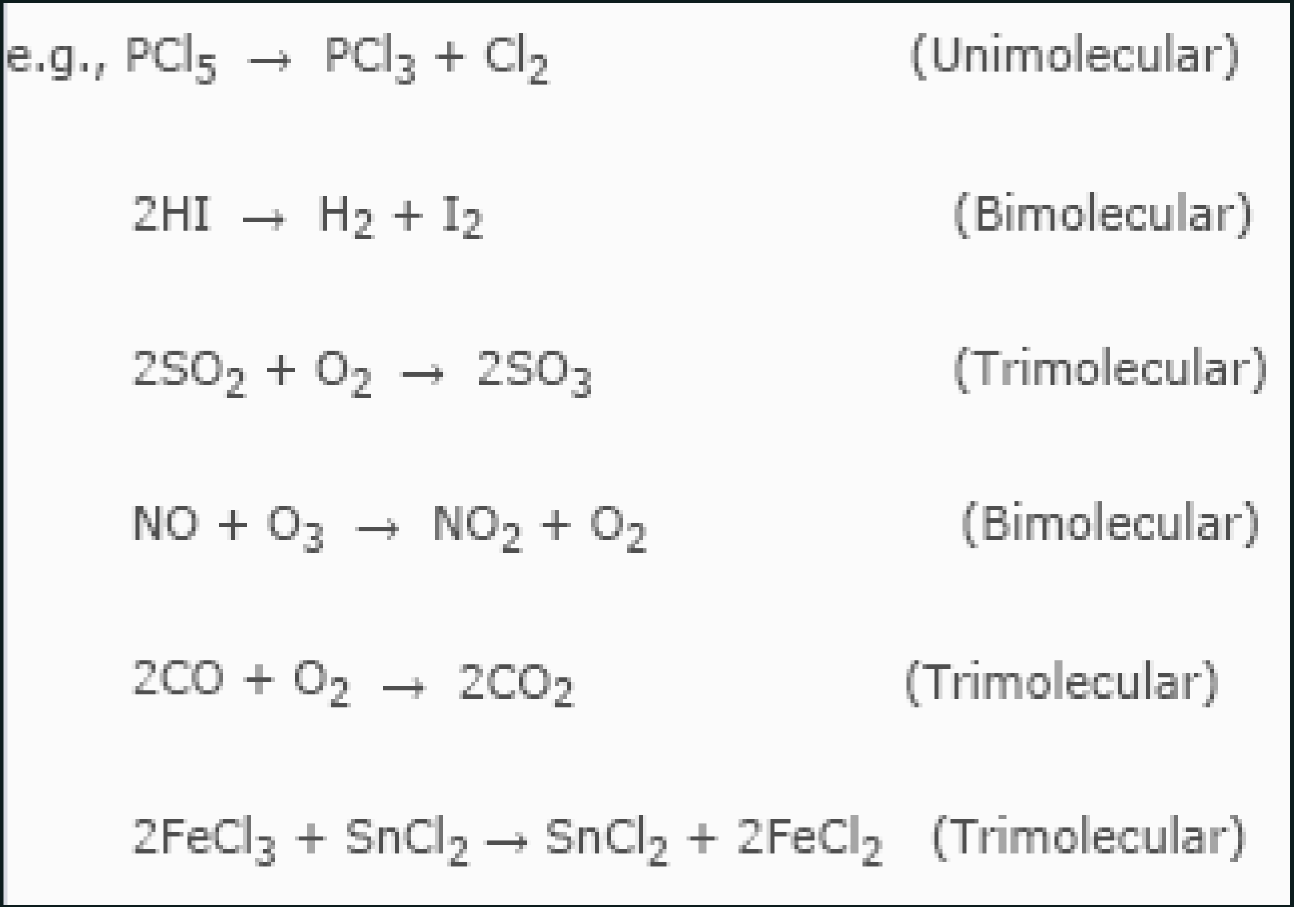
- If a chemical reaction has more than one consecutive stage, then the kinetics are limited by the slowest stage, which is ‘rate determining’. The molecularity of a reaction is defined as *the number of molecules or ions that participate in the rate-determining stage.* This definition is not quite precise, as in some cases it is not easy to explain the exact meaning of ‘participate’. All reactions pass through a transition state. If this is accepted, then the best definition of molecularity is *the number of molecules or ions from which the transition state is formed.* The molecularity is a **theoretical** quantity in that to evaluate it the mechanism of reaction must be **known** or assumed.

MOLECULARITY OF REACTION

- In general, molecularity of simple reactions = sum of the number of molecules of reactants involved in the balanced stoichiometric equation.

OR

- The molecularity of a reaction = the number of reactant molecules taking part in a single step of the reaction.



e.g., $PCl_5 \rightarrow PCl_3 + Cl_2$	(Unimolecular)
$2HI \rightarrow H_2 + I_2$	(Bimolecular)
$2SO_2 + O_2 \rightarrow 2SO_3$	(Trimolecular)
$NO + O_3 \rightarrow NO_2 + O_2$	(Bimolecular)
$2CO + O_2 \rightarrow 2CO_2$	(Trimolecular)
$2FeCl_3 + SnCl_2 \rightarrow SnCl_2 + 2FeCl_2$	(Trimolecular)

- Rate-determining step (RDS) is the slowest elementary reaction in the mechanism and **controls the overall rate** of the reaction.

e.g. $A + 2B \rightarrow D + E$

mechanism: $A + B \rightarrow C + E$ *fast*

$B + C \rightarrow D$ *slow – rate determining step*

$A + 2B \rightarrow D + E$

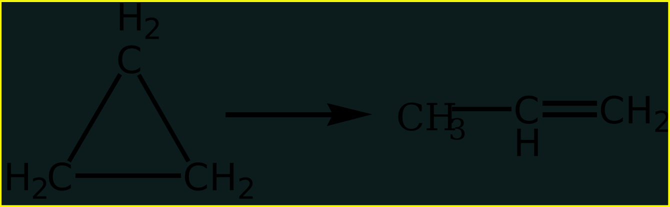
C **is an intermediate** – formed, and then used up in the reactio

Molecularity

- Molecularity is the number of molecules coming together to react in an elementary step.
- Elementary reactions are simple reactions (described by molecularity)

(a) A $\longrightarrow$ Products UNI-molecular reaction

e.g.



(b) A + A $\longrightarrow$ Products or A + B $\longrightarrow$ Products Bi-molecular

e.g. $CH_3I + CH_3CH_2O^- \longrightarrow CH_3OCH_2CH_3 + I^-$

(c) 2A + B $\longrightarrow$ P or A + B + C $\longrightarrow$ P Tri-molecular

Molecularity $\neq$ Order of reaction

- Reaction order is determined by experiment only
- Reaction order is an empirical quantity (values range -2 to 3).
- Can be fractional – found mainly in gas phas
- Can be negative,

$$Rate = k[A]^{-m}[B]^{n} = \frac{k[B]^{n}}{[A]^{m}}$$

A is an inhibitor (decreases the rate)

- In contrast to the order, the molecularity is necessarily a small whole number and cannot be zero or fractional. The terms ‘unimolecular’ and ‘bimolecular’ are used to describe reactions which have a molecularity of one and two respectively .
- In many cases the order and molecularity are equal, for example bimolecular reactions are usually of second order if the reaction occurs in one stage.

  Thus the thermal decomposition of hydrogen iodide

  $$2HI \rightarrow H_2 + I_2$$

  is a second order bimolecular reaction, and the thermal decomposition of tertiary butyl alcohol

  $$t\text{-}C_4H_9OH \rightarrow C_4H_8 + H_20$$

  is a first order unimolecular reaction. On the other hand, the reaction of iodine with acidified aqueous acetone

  $$CH_3COCH_3 + I_2 \rightarrow CH_3COCH_2I + HI$$

  is bimolecular and of zero order. The oxidation of nitric oxide

  $$2N0 \mathbf{+0_2} \rightarrow 2N0_2$$

  is bimolecular and of third order.

HALF-LIFE (**$t_{½}$**)

- *Half-life - the time taken for* 50 % of the *reaction to occur*. It is widely used in describing the rates of radioactive decay in which the half-life is independent of the amount of material present . In general the half-life depends upon the *initial concentrations* as well as upon the *rate constant.* If there is more than one reactant, then a precise value cannot be given to the half-life unless a particular reactant is stated. For example, in a bimolecular second order reaction between A and B, if the initial concentrations are in the ratio of 3 to 2 then:
- at the half-life of A, 75 per cent of B has reacted at the half-life of B, 33.3 per cent of A has reacted.

INTEGRATION OF THE RATE LAWS

- In practice dx/dt cannot be measured directly, since the result of analyses at various times will give a series of values of concentration (x) corresponding to various times **(t).** There are, however, two methods that might be employed to derive the rate constant of the reaction.

- The first method is to plot a graph of (x) against (*t* **)** and measure the slope of the curve at various values of x. This gives dx/dt which can then be substituted directly into the rate law to give the rate constant. For example, if the rate law is dx/dt = *k(a* — x)
-

$$k = \frac{dx/dt}{(a - x)}$$

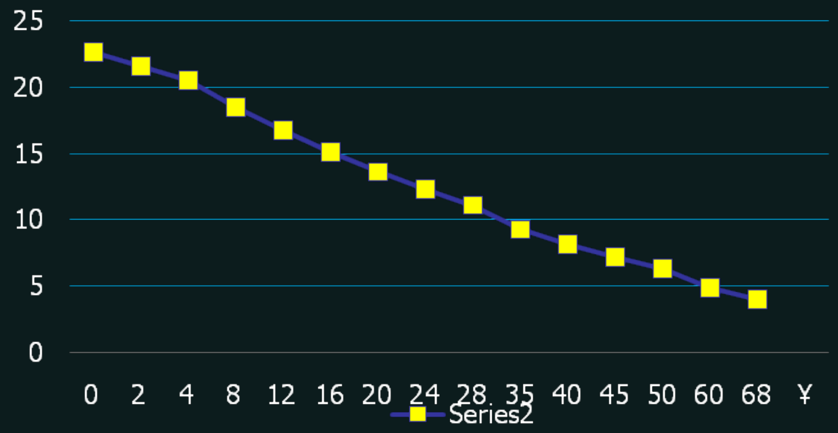
(s d problem using this equation)

- Calculations of a first order rate constant from the differential rate law.
- The decomposition of benzene diazonium chloride in water at 40°C

$$C_6H_5Cl + H_2O \quad = \quad C_6H_5OH + HCl + N_2$$

log (P∞ - P)	P∞ - P	pressure cm xylene	Time in minutes
1.35	22.62	0.00	0.00
1.33	21.55	1.07	2.00
1.31	20.47	2.15	4.00
1.27	18.48	4.14	8.00
1.22	16.73	5.89	12.00
1.18	15.10	7.52	16.00
1.13	13.62	9.00	20.00
1.09	12.30	10.32	24.00
1.05	11.10	11.52	28.00
0.97	9.29	13.33	35.00
0.91	8.15	14.47	40.00
0.86	7.20	15.42	45.00
0.80	6.34	16.28	50.00
0.69	4.88	17.74	60.00
0.60	4.02	18.60	68.00
0.00	0.00	22.62	infinity

Decomposition of benzene diazonium chloride at 40 C in water



- The objection to the general use of this method, which is mathematically simple, is that it lacks in accuracy because of the difficulty of measuring the slope of a curve. This difficulty is accentuated if the curve is not completely smooth due to experimental errors in some of the points.

  The numerical measurement of the slope of the curve is avoided, in the second method, by integrating the rate equation before the experimental results are substituted into it. This converts the rate law from the differential form to an equation of the type

  $kt =$ function of x = F(x), say equation 2.2

- Using the function F(x) derived for the appropriate order of reaction, *k* can be found directly by substituting values of x and **t** into equation (2.2).

  Small experimental errors can be dealt with by plotting a graph of F(x) against **t** and (either visually, or by the method of least squares) drawing the best straight line through the origin and the points. This is a straight line equation, the slope of the line is equal to *k.*

ZERO ORDER REACTIONS

- These reactions are not common, but they do occur in some *heterogeneous* systems and in some solutions . The appropriate rate law for a zero order reaction is
  rate = constant
  or, in mathematical symbols, equation 2.3

$$\boxed{\frac{dx}{dt} = k}$$

- where x is the concentration _of product formed.
  Integrating with respect to t
  x = *kt* + constant
  Since x = 0 when **t =** 0 (i.e. at the beginning of the reaction, no product has formed) the constant must be zero. Hence
  x=kt *equation 2.4*

The dimensions of *k* are concentration /time, i.e. mol l^{-1} s^{-1}.

- To calculate the half-life of this reaction the condition that $t = t_{1/2}$ when $x = a/2$ (a being the initial concentration of the reactant) is substituted into (2.4) to give
- $a/2 = kt_{1/2}$ equation 2.5
- Thus in a zero order reaction the half-life is proportional to the initial concentration of the reactant.

FIRST ORDER REACTIONS

- These reactions are common and are often observed in solution where the solvent happens to be one of the reactants. Many gas phase reactions and radioactive decay processes also obey the first order rate law

$$\frac{dx}{dt} = k(a - x)$$

equation 2.6

Rearrangement gives:

$$\frac{dx}{(a - x)} = k \, . \, dt$$

..............................equation 2.7

- Integrating the last equation, we obtain:

  — Ln (a — x) = *kt +* constant.

- When t = 0, x = 0 and hence

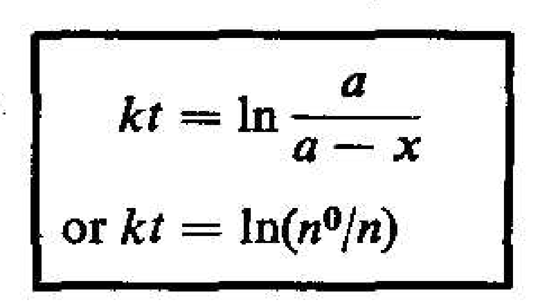
  — Ln a = constant.

- Substituting for the constant in the equation, we get

  $\ln a - \ln (a - x) = kt$ equation 2.9

This equation can be written as:

where n^0 is the initial number of atoms or molecules of the reactant and n is the number remaining at time t. It will be seen from (2.10) that the value of k depends only on the ***ratio*** of two concentrations, the dimensions of k being l/time, e.g. s'. The important practical point that follows from this is



$$kt = \ln \frac{a}{a - x}$$

$$\text{or } kt = \ln(n^0/n)$$

Equation 2.10

- Thus the first order reaction
- $RBr + C_2H_5OH \rightarrow ROC_2H_5 + HBr$
- (where R is an alkyl group) can be followed by removing aliquots, cooling them rapidly and titrating the liberated HBr with alkali. The concentration of the alkali is not needed in order to find *k*, since the ratio a/(a — x) which is required in (2.10) can be expressed as the ratio of two titrations. If T is the titration after 'infinite' time and T is the titratio then :

$$\frac{a}{a-x}=\frac{T_{\infty}}{T_{\infty}-T}$$

- First order reactions have another important property which is that the half-life (i.e. the time for 50 per cent reaction) does not depend on the initial concentration. This may be seen by substituting in (2.10) the conditions for the half-life, namely that when $t = t_{1/2}$, $x = a/2$, hence

$$\ln 2 = \boldsymbol{kt}$$

i.e

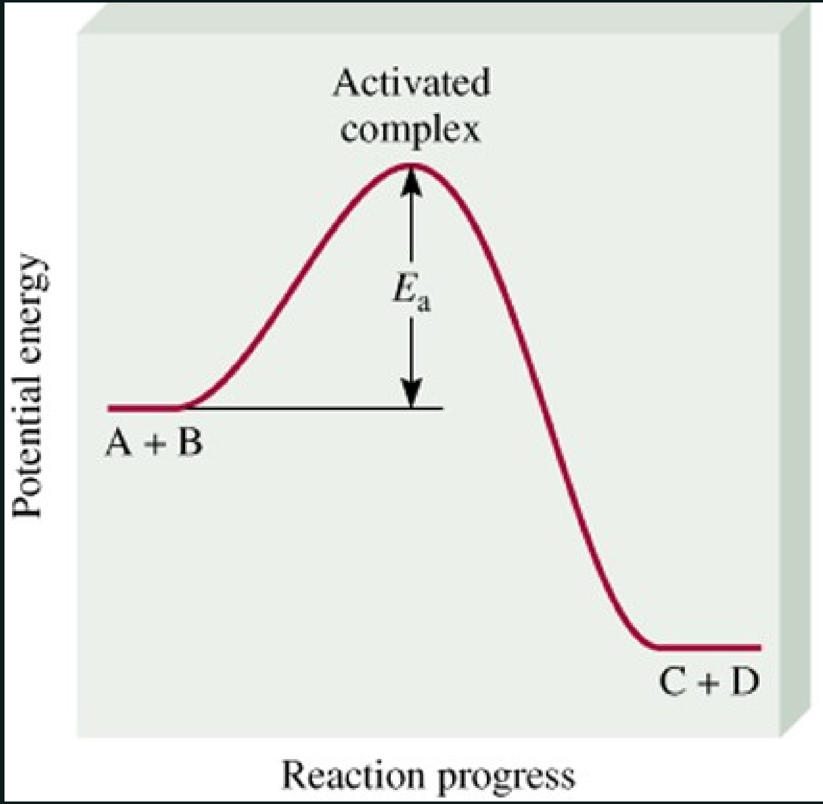
$$\boxed{t_{\frac{1}{2}} = \frac{\ln 2}{k} = \frac{0{\cdot}6932}{k}}$$

- **The half-life is thus independent of the initial concentration of the reactants. In other words, provided a reaction obeys strictly the first order equation, the time for 50 per cent reaction cannot be changed by altering the initial concentration.**
- ***Industrially, this means that the batch time cannot be decreased by increasing the concentration of the reactants***

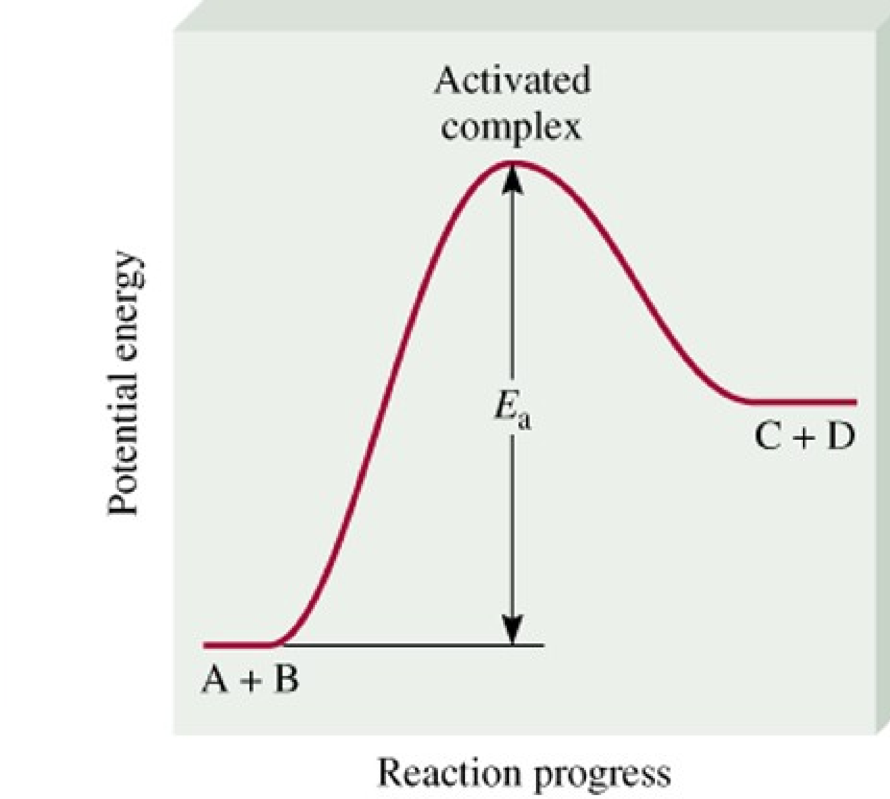
Summary of the Kinetics

Order	Rate Law	Concentration-Time Equation	Half-Life
0	rate = k	$[A] = [A]_0 - kt$	$t_{½} = \frac{[A]_0}{2k}$
1	rate = $k\,[A]$	$\ln[A] = \ln[A]_0 - kt$	$t_{½} = \frac{\ln 2}{k}$
2	rate = $k\,[A]^2$	$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$	$t_{½} = \frac{1}{k[A]_0}$

$$A + B \longrightarrow C + D$$



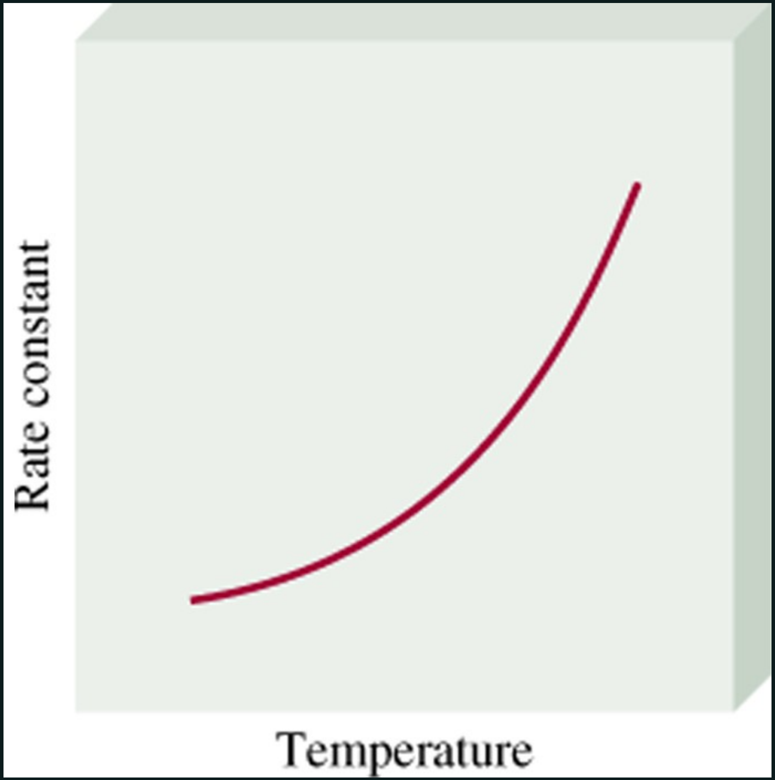
Exothermic Reaction



Endothermic Reaction

The ***activation energy (E_a)*** is the minimum amount of energy .required to initiate a chemical reaction

Temperature Dependence of the Rate Constar



$k = A \bullet \exp(-E_a/RT)$

(Arrhenius equation)

E_a is the activation energy (J/mol

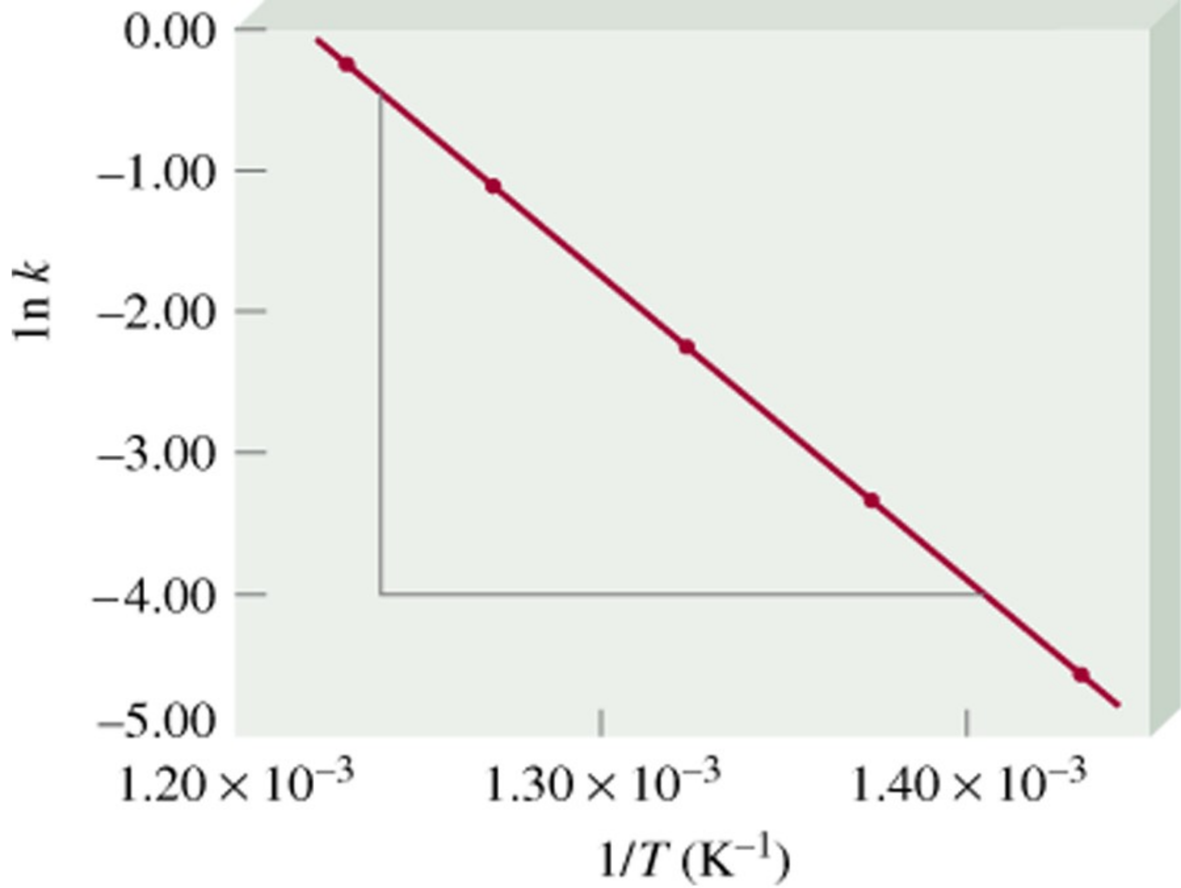
R is the gas constant (8.314 J/K•mol)

T is the absolute temperature

A is the frequency factor

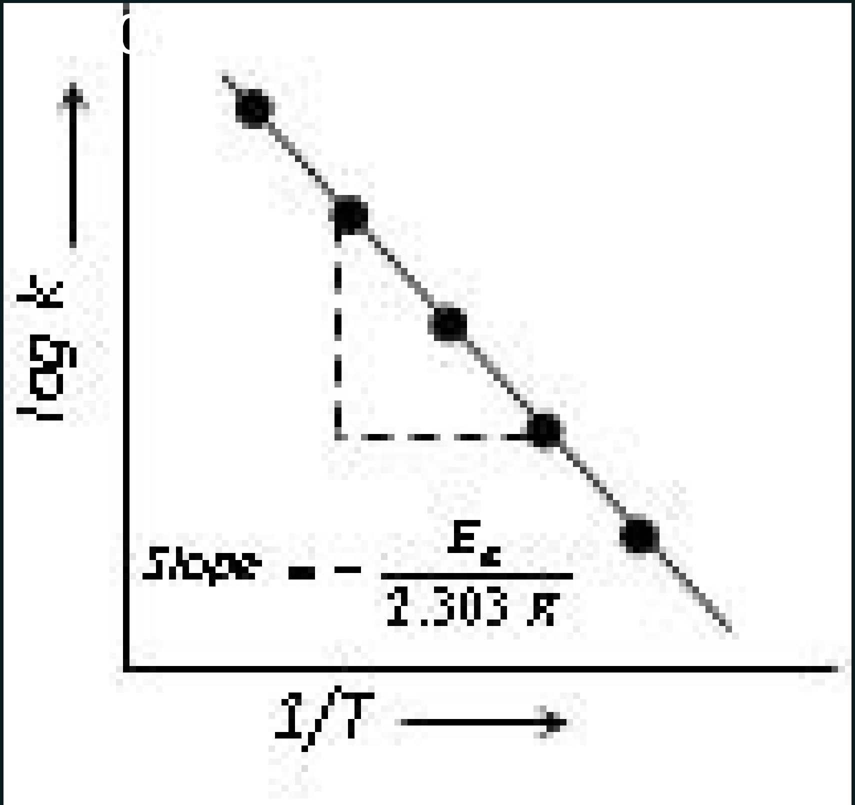
$$- = \ln k \frac{E_a}{R} \frac{1}{T} \quad \ln A +$$

$$- = \ln k \frac{E_a}{R} \frac{1}{T} \ln A +$$



When log *k* plotted against 1/T , we get a straight line. The intercept of this line is equal to log *A* and slope equal to –.E_a/2.303R

.Therefore E_a =



Rate constants for the reaction at two different , temperatures T_1 and T_2

$$\log k_2/k_1 = E_a/2.303R\ [1/T_1 – 1/T_2]$$

where k_1 and k_2 are rate constant at temperatures T_1 . and T_2 respectively ($T_1 > T_2$)